REMARKS/ARGUMENTS

Claims 1-7, 12 and 21 have been canceled. Claims 17-20 and 22-32 are active in the case. Reconsideration is respectfully requested.

Applicants' representative wishes to thank Examiner Cooney for the helpful and courteous interview of February 12, 2008 concerning the above-identified application. As a result of the discussion it is believed that the prosecution of the application has been materially advanced.

The present invention relates to a process for producing flexible polyurethane foams from polyether alcohols based on renewable materials.

Claim Amendments

Claims 1-7 have been canceled in favor of new Claims 22-30. Further, support for the amending language in new Claim 22 with regard to the VOC and FOG values of the foamed product and the maximum odor values of the polyether alcohol can be found in the specification at page 3, line 42 to page 4, line 30. New dependent Claims 31 and 32 are supported by the same pages of text. Accordingly, the amendments that have been made do not introduce new matter into the case. Entry of the amendments and new claims into the record is respectfully requested.

Claim Objection and Rejection, 35 USC 112

A copy of the Daimler/Chrysler test method for the determination of FOG and VOC values that are mentioned on page 4 of the text is enclosed in support of the subject matter newly incorporated into Claim 22 and the subject matter of Claims 31 and 32. The description is in the English language.

Claim Rejection, 35 USC 103

Claims 1-7 and 15-21 stand rejected based on 35 USC 103(a) as obvious over Sugiyama et al, U. S. Patent 6,313,060 in view of JP-05163342. This ground of rejection is respectfully traversed.

As discussed by applicants' representative at the interview, the Sugiyama et al patent discloses a resilient polyurethane foam which employs a polyether polyol that can be produced by reacting an alkylene oxide with a monol or a polyhydroxyl compound that has from 2 to 8 hydroxyl groups in a ring opening polymerization reaction. Among other catalysts, the reaction can be preferably catalyzed by a cyanometallate catalyst such as those mentioned in column 5, lines 8-14 of the patent (double metal cyanide). Various monols and polyols are described at column 8, lines 30-42. Suitable polyols mentioned include the likes of some glycols, triols, sorbitol, dextrose and the like. However, nowhere mentioned are what is termed as renewable raw materials in the present claims which react with alkylene oxide under ring opening polymerization conditions, which reaction is catalyzed by a DMC catalyst. Subsequently, the polyether polyol that is formed is reacted with a polyisocyanate to form the desired flexible polyurethane foam. In failing to disclose renewable raw materials, Sugiyama et al fails to make mention of previous work in this area of employing renewable raw materials as a source material for the preparation of polyurethane foams and the problem of emissions of volatile materials and odors encountered during the manufacturing process. These problems have limited the usefulness of polyurethane foams that are formed from renewable raw materials. However, the discovery of the present invention is that when a DMC catalyst, specifically, is used to catalyze the ring-opening polymerization reaction of alkylene oxide with a renewable raw material to form a compound that contains at least two hydrogen atoms, quite unexpectedly, the resulting polyetherpolyol exhibits notably reduced unpleasant odor as shown by the data of the examples of the application, particularly a

comparison of the odor evaluation data of the polyetherpolyol products of the invention of Examples 1-3 where a DMC catalyst was employed as the catalyst and Comp. Exs. 4 and 5 where a conventional catalyst, i.e., KOH, was employed as the polymerization catalyst. The superior odor reducing property of the polyether polyol of the present invention is identified in terms of specific maximum values in new Claims 22 (an upper limit value of 2.0) and 31 (an upper limit value of 1.7). Further, the improved low-emission polyurethane foams of the present invention are signified in present Claims 22 and 32 by incorporating the defining maximum limits of FOG (emissions of condensable compounds) and VOC (volatile organic compounds) in the claims as 200 ppm (100 ppm) and 100 ppm (50 ppm) respectively. Applicants submit that it is clear from the present claims as amended that the polyurethane foam of the present invention is not shown or suggested by Sugiyama et al.

The deficiencies of the Sugiyama et al patent are believed to be neither overcome nor improved upon by the cited '342 reference. The abstract of the '342 reference discloses the preparation of a polyether by the catalyzed ring-opening reaction of an epoxide (alkylene oxide) and castor oil in the presence of a DMC catalyst. Most of the disclosure of the reference is concerned with aspects of the preparation of the polyether. The reference makes only the briefest remark in paragraph [0028] of the reaction between the polyether product and an isocyanate to prepare a polyurethane product. Absolutely nothing is mentioned about the renewable raw materials of the present claims, other than castor oil, and nothing is said as to the problems encountered in attempting to use renewable raw materials as a coreactant with epoxide to form a polyether polyol for reaction with a diisocyanate compound in order to prepare a foamed polyurethane product. In fact, the "problem solved" in the '342 reference as stated in paragraph [0006] is that when castor oil is used as an initiator (for preparation of the polyether polyol), decomposition of unsaturated bonds in the molecules of the oil can occur as well as ester bond formation, conventional alkali and acidic catalysts can not be used

to catalyze the polymerization reaction. The inventors of the patent have found that the problem of an acceptable catalyst is solved when a metallocyanide complex compound is used as the catalyst for the polymerization reaction. Accordingly, it is believed that the cited combination of references does not suggest the invention as claimed and withdrawal of the rejection is respectfully requested.

It is now believed that the application is in proper condition for allowance. Early notice to this effect is earnestly solicited.

Respectfully submitted,

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NFO:FDV

Analysis of the emission of volatile and condensable substances from vehicle interior materials by thermodesorption

PB VWL 709

0 Circulation

Plant 50	VWL Teams,	VWK
Plant 54	QWO	
Plant 67	QST	

1 Objective

The purpose of this analytical method is to determine emissions from materials used in vehicle interiors.

2 Scope

DaimlerChrysler, Mercedes-Benz product line

3 Terms

Emissions, interior trim materials, vehicle interior air, thermodesorption analysis (TDSA), VOC value, Fog value.

4 Responsibilities

PWT/VWL, Organic Analysis Team

5 Description

Vehicle interior materials are characterized according to the type and quantity of organic substances that can be stripped from them.
Two cumulative values are determined to this end, from which the emission of volatile substances (VOC value) and the condensable content (fog value) can be estimated. Individual emission substances are also identified.
During analysis the samples are thermally desorbed and the emissions separated out by gas chromatography and detected by mass spectroscopy.

6 Applicable documents

DBL 8585, List of MAC and BAT values (DFG)

7 Appendices

	File names
1. Notes on weighed amounts and preparation of samples	*PBVWL709Anl1.doc*
2. Production of paint samples	*PBVWL709Anl2.doc*
3. Excel report template	*PBVWL709Anl3.doc*
4. Sketch of thermodesorption analysis	*PBVWL709Anl4.doc*
5. Sample chromatogram for control test mixture	*PBVWL709Anl5.doc*
6. Limiting/target values	*PBVWL709Anl6#2.doc*

Issued : 2001-01-11 Replaces : 2000-07-19 File : PBVWL709#2_eng	Author: Kante	Approved: Dr.Munz

Contents

1 General notes, definitions and organization of contract

1.1 Materials to be tested, relevant vehicle interior area in relation to emissions

All materials that can contribute to emissions in the vehicle interior must be tested. Examples include emissions from textiles, carpets, adhesives, sealants, foams, plastic components, films, leather, interior paints and composite materials.
The relevant vehicle interior area in relation to emissions comprises all areas that are linked to the passenger compartment either directly or by air contact. It also includes the luggage compartment, air-conditioning and heating systems, spaces behind trim, etc.

If there is no difference in the composition of different samples of a material or if the difference in formulation is not expected to influence emissions, it is sufficient to examine representative samples of this component family.
Responsibility for the accuracy of the assumption that emissions are identical lies with the supplier. In case of doubt he should contact his upstream supplier.
For the first sample at least, a laboratory authorized by DaimlerChrysler must perform the VOC/fog analysis. The supplier must send the results to DaimlerChrysler (see section 3.4.5).

1.2 Thermodesorption analysis

In thermodesorption analysis (TDSA) small quantities of material are heated in a glass tube under defined conditions, the volatile substances emitted during the process are transferred to a gas chromatograph in an inert gas stream, where they are first cryofocused at –150°C in the cryogenic trap (liner) of a temperature-programmable evaporator [1].
At the end of the curing phase the liner is quickly heated to 280°C. The focused substances evaporate, are separated out in the gas chromatographic analytical column and then detected by mass spectroscopy.

☞ *Appendix 4 provides a schematic view of the thermodesorption analysis equipment.*

A semi-quantitative determination of the emissions, expressed as mass ppm [2], can be obtained by calibration with reference substances.
Toluene and n-hexadecane are used as reference substances for VOC analysis and the fog value respectively. Unknown substance peaks can be identified from the mass spectra and the retention time.

[1] Here: = **Cold injection system** (CIS) = Temperature-programmable injector for gas chromatograph
[2] **ppm** = parts per million = µg of substance per g of weighed portion that are stripped + detected under these conditions. It is not a measure of content.

1.3 VOC value [3] (according to PB VWL 709)

The VOC value is the sum of volatile to moderately volatile substances. It is calculated as toluene equivalent.

In the method described here, substances in the boiling or elution range from pentane (C5) to eicosane (C20) or thereabouts are identified and evaluated.
It is assumed that these substances can be detected from an analysis of the vehicle interior **air**.
Determination is performed by curing the sample for 30 minutes at 90°C. The VOC value is measured as a double value.
The higher of the two values is cited as the result.

1.4 Fog value

Following VOC analysis the fog value is determined by leaving the second sample in the desorption tube and curing it for a further 60 minutes at 120°C.

The fog value is the total of highly volatile substances that elute from n-hexadecane from the retention time onward. It is calculated as hexadecane equivalent.

Substances with boiling points up to at least n-alkane C32 are detected.
These substances can readily condense at room temperature and make a substantial contribution to the fogging coating on the windshield.

The limits for the VOC and fog range have been established by convention. They have been derived empirically from numerous analyses of vehicle fogging condensates.
According to these analyses, fogging consists primarily of substances that boil above around 280°C (boiling point of n-hexadecane = 286°C).

1.5 Evaluation of emitted substances

Reference is made to the latest list of MAC values[4] and to DBL 8585 in order to evaluate the toxicity of the substances identified. Substances listed in the following categories should be rated as critical:

Category	Classification
Carcinogenic	K1, K2, K3 A, K3 B
Pregnancy	A, B
Mutagenic	1, 2, 3 A, 3 B
Allergic effect	H,S

[3] **VOC value** = volatile organic compounds
This VOC value refers exclusively to the method described here and is not comparable with VOC values obtained using other methods.
[4] **List of MAC and BAT values**, issued by: Deutsche Forschungsgemeinschaft, Wiley-VCH-Verlag

If substances of this type are detected, they must be explicitly identified in the analysis report.
Substances that are assumed or known to be potentially harmful due to their physiological properties (e.g. odor, irritation to mucous membranes) must also be rated as critical.
The same applies to substances that can be regarded as precursors of other critical compounds or that are known allergens, e.g. carcinogenic nitrosamines can form from aliphatic secondary amines.

Limiting values for VOC, fog and individual substances are set out in Appendix 6.

1.6 When is VOC/fog analysis required?

1.6.1 Sample approval/development

The relevant supply specifications state whether material testing is necessary along with any requirements that exist.
Generally speaking, the results of the thermodesorption analysis must be submitted together with the first sample test report for first and new sample approvals.

For coordination purposes the supplier must submit a VOC/fog result from the Institut Fresenius[5] for the **first sample test report**.

For the sample approval of materials comprising various components, analyses already arranged by upstream suppliers can be submitted.

In the context of the preliminary development of materials, a decision can be made by agreement with the team responsible for the material regarding the stage of development beyond which an analysis is reasonable.

1.6.2 Standard monitoring

In the context of standard monitoring of approved products, a simple determination of the overall VOC and fog value, in other words no analysis of individual peaks, is all that is required. This must be arranged by the supplier at appropriate test intervals and documented. A visual comparison with the approved chromatogram is sufficient to check for any substantial changes, e.g. additional new substances.

[5] Address: Institut Fresenius, Chemische und Biologische Laboratorien GmbH
Dr. Krüger
Hauert 9
44227 Dortmund
Germany
Tel. +49 (0)231/758960

1.6.3 Formulation changes

New sample approval is required under all circumstances in the event of changes to the formulation that could worsen emissions.

1.6.4 Complaints

In the event of complaints about materials relating to the question of emissions, thermodesorption analysis may help to identify the cause.
Details of a complaint analysis should be agreed with the DaimlerChrysler team in charge.

1.7 Timing of sampling/preparation/dispatch

The time at which a sample is taken for analysis must be chosen such that the age of the material corresponds to the shortest possible delivery time for the component to the DC final assembly plant.
Example:
A foamed material is generally delivered to the car plant within 2 to 12 days after foaming. Analysis must therefore be performed on a foam sample that has been allowed to evaporate for a maximum of 2 days.
The worst-case scenario must always be assumed.

A representative sample of size DIN A5 or thereabouts is taken for analysis. It must not become contaminated. Each sample is completely wrapped in an airtight package comprising two layers of thick aluminum foil (30 µm), the edges of which are folded several times. The sample is also sealed in a polythene bag and can then be sent to the laboratory. It is then stored at a maximum of –18°C until it is analyzed.

Further details of the handling of the material for analysis and the preparation of the sample are provided in Appendices 1 + 2.
Appendix 1: Determining the weighed amount of different material samples.
Appendix 2: Specifications for the production of paint films.

1.8 Presenting the results of the analysis

The contracted laboratory prepares a written analysis report containing the VOC and fog value together with a list of the substances detected. The substances are quantified and compared with the current MAC list.
The component supplier sends DaimlerChrysler the written laboratory report, comprising the GC report, chromatograms for the VOC and fog analysis, and all raw data from the analysis (on CD-ROM), for inspection.

2 Analysis parameters

2.1 Instrument system

The analytical method described in this report was performed with the following instrument system:

Instrument	Model/manufacturer
Thermodesorption system	TDSA (with auto sampler), Gerstel, glass desorption tube, external diameter = 6 mm, internal diameter = 4 mm
Gas chromatograph (GC)	HP6890 with electronic pressure regulation, Agilent (Hewlett Packard)
Cryogenic trap	Cold injection system KAS 3, Gerstel, glass liner: smooth type, filled with deactivated quartz wadding (cat. no. 842010)
Mass spectrometry detector (MSD) Evaluation software	HP5972A, Agilent (Hewlett Packard) Chemstation G1701BA MS Excel 97, Wiley275/Nist MS spectra library

Notes:

Attention

Transferability of results cannot be assumed if different thermodesorption/GC systems are used. It must be checked in each case.
In some circumstances the quantity emitted is substantially dependent on the constructional features of the individual analytical instrument system. For example, the geometry of the sample chamber, the length of the heated zone, the length of the transfer line, the type of pneumatic regulation or different flow conditions, may influence the result.

DaimlerChrysler Test Instructions
Sindelfingen Plant

Analysis of the emission of volatile and condensable substances from vehicle interior materials by thermodesorption PB VWL 709

2.2 Device parameters for the VOC analysis run

2.2.1 Thermodesorption unit (TDSA) parameters for the VOC analysis run

Sample mode	Sample removal
Flow mode	Splitless[6]
Initial temp.	20°C
Delay time	1 minute
1st rate	60 K/min.
1st final temp.	90°C
1st final time	30 minutes
Transfer line to CIS	280°C
GC run time	67 minutes

2.2.2 Cryogenic trap (cold injection system, KAS 3) parameters for the VOC analysis run

Flow mode	Split 1:30
Initial temp.	-150 °C
1st rate	12 K/ sec
1st final temp.	280°C
1st final time	5 minutes
Equilibration time	1 minute

2.2.3 Gas chromatograph (GC) device parameters for the VOC analysis run

Transfer line to MSD	280°C
Carrier gas	Helium 5.0, post-purified
Flow rate	1.3 ml/min.
Pneumatics (EPS)	Constant flow mode
Analytical column	50 m x 0.32 mm, 0.52 µm 5% phenylmethyl siloxanes HP Ultra 2 (19091B-115)
Oven temperature program:	40°C, 2 min. isothermal, 3 K/min. to 92°C 5 K/min. to 160°C 10 K/min. to 280°C,
(Total run time: approx. 59 minutes)	10 min. isothermal

2.2.4 Mass spectrometer settings (MSD) for the VOC analysis run

Start of data recording	After 3.0 minutes
Calibration of mass axis	Standard spectra autotune *(measured at oven temp. of 100°C)*
Scan mode (low/high mass)	29-280 amu, at 3.1 scans/s
MS threshold	100

Note: The chromatographic integration conditions must be selected so that 1 ppm peaks can be detected reliably.

[6] For technical reasons a forced split flow of approx. 3 ml/min nevertheless occurs here.

2.3 *Device parameters for the fog analysis run*

2.3.1 Thermodesorption unit (TDSA) parameters for the fog analysis run

Sample mode	Sample removal
Flow mode	Splitless
Initial temp.	20°C
Delay time	1 minute
1st rate	60 K/min.
1st final temp.	120°C
1st final time	60 minutes
Transfer line	280°C
GC run time	57 minutes

2.3.2 Cryogenic trap (cold injection system KAS 3) parameters for the fog analysis run

Flow mode	Split 1:30
Initial temp.	-150 °C
1st rate	12 K/ sec
1st final temp.	280°C
1st final time	5 minutes
Equilibration time	1 minute

2.3.3 Gas chromatograph (GC) device parameters for the fog analysis run

Transfer line to MSD	280°C
Carrier gas	Helium 5.0, post-purified
Flow rate	1.3 ml/min.
Pneumatics (EPS)	Constant flow mode
Analytical column	50 m x 0.32 mm, 0.52 µm 5% phenylmethyl siloxanes HP Ultra 2 (19091B-115)
Oven temperature program: (Total run time approx. 48 minutes)	50°C, 2 min. isothermal, 25 K/min. to 160°C 10 K/min. to 280°C, 30 minutes isothermal

2.3.4 Mass spectrometer settings for the fog analysis run

Start of data recording	After 12.5 minutes
Calibration of mass axis	Standard spectra autotune *(at oven temp. of 100°C)*
Scan mode (low/high mass)	29-370 amu, at 2.3 scans/s
MS threshold	100

The chromatographic integration conditions must be selected so that 1 ppm peaks can be detected reliably.

3 Method of analysis

3.1 *Cleaning the glass desorption tubes*

Only glass tubes that are completely free from contamination may be used. Even brand-new desorption tubes must be thoroughly cleaned before being used for the first time.
The tubes must be cleaned by storing them for several hours, ideally overnight, in an alkaline cleaning solution[7].
They must then be rinsed thoroughly, first under hot running water for at least one minute, then with demineralized water.
The tubes are then dried in a drying oven (approx. 45 minutes at 105°C) and stored free from contamination (wrapped in aluminum foil in an airtight package) until use.

3.2 *Testing the system*

The function of the instrument system is tested by analyzing a standard control solution within the sample series (see 3.2.1).
The standard control solution contains non-polar, polar basic and acid components that would display a noticeable peak tailing even with low adsorption effects.
This process can also be used to check for substance losses due to leaks.
Peaks occurring in close succession, such as o-xylene and n-nonane, can be used to check the separation efficiency of the chromatographic column. These two substance peaks must be virtually baseline-separated under the chosen chromatographic conditions.

The performance of the mass spectroscopy detector is checked by means of mass and sensitivity tuning (standard spectra autotune in the case of HP instruments), and the specifications required by the manufacturer must be achieved. An air/water check must also be performed to test the integrity of the entire system.

All substances in the control mixture must be clearly identified in the mass spectra library (e.g. Wiley 275) during the search run.

The TDSA/GC system must also be checked for possible memory effects by performing a dummy run with an empty desorption tube at least before every sample series.
If negative effects such as severe peak tailing, disruptive dummy run peaks or significant loss of substance occur, the system must be cleaned. The GC column, CIS liner, transfer line or seals may need to be replaced.
We recommend documenting the results of the control run for each sample series as part of quality control procedures (control card). The peak area ratios, concentrations as toluene equivalents and retention times can be used as control quantities.

3.2.1 Preparing the control solution

[7] The alkaline laboratory glass cleaner SODOSIL RA8 (Riedel-deHa?n) has proven effective.

The following substances dissolved in methanol have proven to be suitable for use as the system control (listed in elution sequence under VOC conditions):

Table 1 Control mixture

benzene	2-ethylhexanol-1
n-heptane	n-undecane
toluene	2,6 dimethylphenol
n-octane	n-dodecane
n-butyl acetate	n-tridecane
p-xylene	n-tetradecane
o-xylene	dicyclohexylamine
n-nonane	n-pentadecane
n-decane	n-hexadecane

220 ± 20 mg of each component are weighed into a glass vessel (e.g. 5 ml roll-edged glass) to an accuracy of 0.1 mg. Approx. 100 mg of this mixture are transferred to a 50 ml measuring flask and weighed (weighing accuracy ± 0.1 mg). Methanol (p.a.) is then added to just below the calibration mark on the measuring flask, the flask is closed and carefully shaken until all solvent droplets have fully dissolved in the methanol. The measuring flask is then filled up to the calibration mark and shaken again.

4 µl of this solution are then injected into a Tenax desorption tube for the control run (as described in section 3.3.2).
This means that the desorption tube contains approx. 0.45 ± 0.05 µg of each substance.

The retention times for the n-alkanes present in this mixture are a suitable reference point for determining the retention index of unknown substance peaks and can therefore be used as an additional check for MS identification during the sample runs.

3.2.2 Stability of the control solution

Apart from the *n-butyl acetate* component, the control solution can be kept for several weeks if stored correctly (refrigerated at 8°C maximum). Butyl acetate hydrolyzes noticeably within a few days, however. An additional butanol and acetic acid peak occurs in the chromatogram and the butyl acetate peak becomes correspondingly smaller. In this case the control solution must be repeated with a fresh batch in order to evaluate the butyl acetate peak.

3.3 Calibration

Calibration is performed using the external standards method.
This method involves charging separate desorption tubes containing *Tenax TA* with the individual calibration solutions.

3.3.1 Calibration solutions

Two calibration solutions are required:

1. For the VOC analysis approx. 0.5 µg/µl toluene (p.a.) in methanol (p.a.)
2. For the fog analysis approx. 0.5 µg/µl n-hexadecane (p.a.) in methanol (p.a.)

Approx. 25 mg (accuracy to ± 0.1 mg) of toluene or n-hexadecane are weighed into a 50 ml measuring flask, the measuring flask is filled with methanol to just below the calibration mark, closed and shaken well. The flask is then topped up with methanol to the calibration mark and shaken again.

The calibration solutions can be stored in a cool place for up to 3 months.
Guaranteeing the accuracy of the concentration is part of the laboratory's quality control procedure.

3.3.2 Charging the calibration or control solution onto Tenax

A desorption tube filled with Tenax TA is connected to an injection device guaranteeing a controlled flow of inert gas (helium 5.0) through the tube while the calibration solution is being added.

Models consisting of septum screw fittings from worn-out GC injectors or a cold injection head fitted with an adaptor and no septum (Gerstel) have proven effective. The advantage of the latter design is that the dead volumes are relatively low, so fewer losses can occur.
A simple adjustable flowmeter should be connected upstream of the injection device to control the helium flow.

A gas meter for controlling the overall volume passing through the injection device and for checking the integrity of the system must be connected downstream of the injection device.

The flow rate should be set to approx. 0.7 ± 0.3 l/min, and the total flow quantity should be around 2.5 – 3 liters. The methanol matrix fed into the system is largely removed, whereas toluene or hexadecane remain on the Tenax.

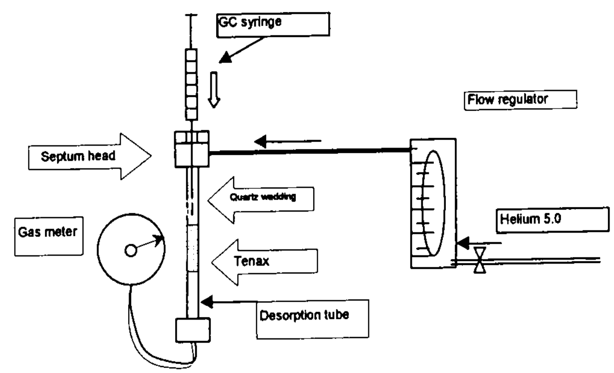
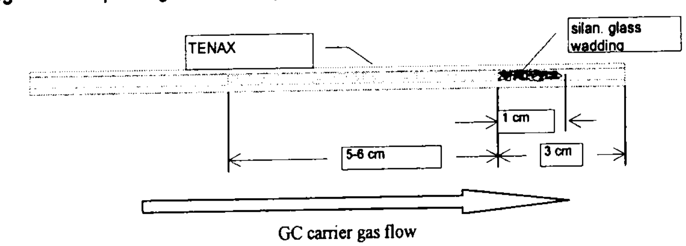


Fig. 1 Equipment for charging the calibration solution

3.3.2.1 Tenax desorption tube:

The Tenax packing must be inserted into the tube in such a way that it can be completely covered by the heating zone of the desorption oven.
For the tubes in the Gerstel TDSA instrument the Tenax packing should be around 5-6 cm in length.
A gap of approx. 3 cm must be left between the Tenax packing and the end of the tube on the transfer line side to prevent the transfer line from protruding into the packing. A plug of deactivated (silanized) glass wadding measuring approx. 1 cm in length, into which the calibration solution is injected, is placed on top of the Tenax layer.

Fig. 2 Tenax packing in the desorption tube



After bringing the calibration solution up to room temperature, 4 µl are drawn up with a 10 µl GC syringe, ensuring that the solution is free from bubbles, and slowly (over approx. 15 seconds) injected into the plug of glass wadding. The inert gas flow is switched on during this process.

Notes:

1. To avoid losses it is advisable to inject the calibration solution directly into the glass wadding plug. Otherwise sizeable fluctuations in the measured values are likely.
2. Tenax can alter over time depending on usage. The quality of the Tenax tubes must be checked by suitable means (e.g. visual check + dummy run). If necessary the packing should be replaced.

3.3.3 Analysis parameters for the calibration and control solution

3.3.3.1 Thermodesorption unit (TDSA) parameters for the calibration run

Sample mode	Sample removal
Flow mode	Splitless
Initial temp.	20°C
Delay time	1 minute
1st rate	60 K/min
1st final temp.	280°C
1st final time	5 minutes
Transfer line to CIS	280°C

3.3.3.2 Cryogenic trap (cold injection system, KAS 3) parameters for the calibration run

Flow mode	Split 1:30
Initial temp.	-150 °C
1st rate	12 K/sec
1st final temp.	280°C
1st final time	5 minutes
Equilibration time	1 minute

3.3.3.3 Gas chromatograph parameters for the calibration and control run

The same parameters are used for toluene calibration and analysis of the control mixture as for the VOC sample run. Only data recording begins later, after approx. 5.5 minutes, in order to mask the methanol peak.

Hexadecane calibration is performed under the same GC conditions as the fog analysis run.

The GC runs can be shortened relative to the sample runs by interrupting the oven temperature program following elution of the calibration substances.

3.4 Sequence of sample analyses

3.4.1 Cutting the samples to size and weighing them into the desorption tubes

For each sample two tubes are filled with the weighed amount specified for the material:

Tube A: First VOC analysis run
Tube B: Second VOC analysis run followed by fog run.

Prior to being weighed, deep-frozen samples must be brought back to room temperature before opening the PE bag to prevent condensation of atmospheric moisture.

The weighed amount of the samples depends on the type of material being tested. It is generally between 10 mg and approx. 50 mg (see Appendix 1).
Required accuracy: ± 0.1 mg.

> **Weighed amount of sample:**
> Weighed amounts of specific materials are listed in **Appendix 1**.

Given the variety of possible sample materials, it is impossible to provide a universal specification for the sizing of samples.
When cutting the sample to size, the aim should be to obtain as coherent and "plane" a size as possible. The aim is **not** to obtain the largest possible surface area by reducing the size. The following procedure should be taken as a guideline:

The desorption tube has an internal diameter of 4 mm which, because of the thickness of the sample, cannot be fully utilized. The temperature-controlled zone of the tube and hence the maximum sample length is around 4 cm.
In order to insert as large pieces as possible, maximum use should first be made of the width of the sample tube when cutting the sample to size. The maximum sample width is generally around 3 mm. The length and thickness of the sample are variable and governed by the specified weighed amount (Appendix 1). It is preferable to cut the sample slightly on the long side and reduce the thickness accordingly.
The sample size should be stated in the report (e.g. L x B x H = approx. 15 x 2.8 x 0.7mm).

A special procedure involving dried films applied to aluminum foil is used for paints and adhesives (see Appendix 1-2).

3.4.2 Calibration run, determining the calibration factors (response factor)

At least two Tenax desorption tubes for each sample series are charged with the toluene or hexadecane calibration solution (see *section 3.2)* and the areas of the calibration peaks determined.
The response factor is calculated as the quotient of the absolute mass (in µg) of toluene or hexadecane that was injected into the tube and the resulting peak areas in each case.

Equation 1

$$Rf = \frac{\mu g\ toluene\ (C16)}{peak\ area} x1000000$$

3.4.3 Quantitative chromatographic evaluation

The total area of all of the substance peaks occurring in the chromatogram (excluding artifacts) is determined first.
The integration parameters for the chromatography software must be set so that peaks with a concentration of ≥1 ppm are still detected reliably.
If the chromatogram includes so-called "oil mountains", consisting of coherent chemically identical isomer mixtures, these are integrated as **one** peak, in which the baseline is laid from the start to the end of the "mountain". If additional and clearly identified peaks of other substance classes occur in this zone, they must be integrated and specified separately.
In order to calculate the concentration, the individual peak areas are multiplied by the response factor (see section 3.4.2)
for toluene, in the case of VOC analysis ,
for hexadecane, in the case of fog analysis

and divided by the appropriate weighed amount of sample:

Equation 2

$$Emission\ [ppm] = Rf(toluene,C16)\ x \frac{Peak\ area[counts]}{1000\ x\ weighed\ amount\ of\ sample\ [mg]}$$

The total concentration from the VOC run calculated as toluene equivalent gives the **VOC value**. The total concentration from the fog run calculated as hexadecane equivalent gives the **fog value**.
If the VOC results deviate by more than 20% relative to the mean value, a repeat analysis, including a fog run, must be performed. Both VOC values must be stated in the test report, but the analysis with the higher value is used for evaluation.

3.4.4 Qualitative analysis

The individual peaks (>1 ppm) are classified on the basis of their mass spectra and – if available – their retention indices (from the literature or reference analyses).
Every MS search run result must be checked for plausibility before being transferred into the results table.
If a substance cannot be clearly identified, a possible suggestion marked with a question mark or a reference to the substance class can be given, provided that appropriate reference points (e.g. typical mass fragments) permit such conclusions to be drawn.

The following convention should be followed for indicating the varying reliability of the substance classification:

Example of notation	Explanation
Toluene, methyl benzene	Mass spectrum and retention of the reference substance are virtually identical (classed as a very reliable identification)
? 1,1-bis (p-toluyl)ethane 210 195 179 104	=> Preceding question mark: No definite classification can be made from mass spectra or retention, but this substance is regarded as a possibility (very similar). Significant mass fragments are cited
?Alcohol, **31** 57 85	=> Question mark + name of substance class: Typical fragments or known fragment samples suggest the substance class
? 54 76 99 109	No conclusions can be drawn about the compound
Isomeric paraffin fraction, boiling range "C16-C26"	In the case of "oil mountains" the substance class should be given as the substance name and the approximate boiling range stated, relative to n-alkanes. The retention-time of the mountain maximum should be entered in the column headed "Retention time"
Cyclohexanone + ?	An identified peak is superimposed by one or more unknown substances
Artifact	Peak that cannot originate from the sample or that has been generated in the system

3.4.5 Results reports/documentation

The chromatography results are transferred to an Excel table containing, as a minimum, the following information about the tested sample:

Header area	Results area
› Exact name of the material tested (material, batch)	› Retention time
› Component name	› Substance name
› Manufacturer's/supplier's name	› CAS number
› Date of manufacture of material	› Percentage of peak
› Analysis date	› Concentration [ppm]
› Weighed amount [mg]	› Comments on peak
› Approximate sample size	› VOC (fog) value
› Part no.	› Second VOC value
	› Comments on analysis

A corresponding Excel template is provided in Appendix 3.

Note regarding the substance name field

Various naming conventions for a substance, such as are commonly suggested in MS libraries, can be copied over directly, but the substance name field should not be overloaded with too many, generally superfluous, names.
It is sufficient to state 1 to 3 "conventional" names in addition to the CAS name.

The chromatograms for the VOC/fog determination and associated substance lists (Excel printout) must be attached to the results report. The full set of analytical data must be supplied on a CD-ROM. It should include:

- 2 raw chromatogram data files for the VOC determination [8]
- 1 raw chromatogram data file for the fog determination
- Raw chromatogram data files for the dummy runs
- Raw chromatogram data files for the calibration and control runs
- Excel files containing the detailed results of the VOC/fog analysis [9]

[8] All raw chromatogram data files must be able to be read by Chemstation MSD software (G1701BA)
[9] Using the DC Excel template (see Appendix 3)

Note:

1. The Agilent Chemstation software transfers the chromatography results to the Excel data format using DDE file transfer. This process and the subsequent calculation of the concentration values can be automated using appropriate Chemstation and Excel macros.

2. For the first sample approval, conventions must be complied with in order to ensure that data can be exchanged with DC systems. Particular information has to be entered in defined Excel cells, for example. The contracting laboratory may need to contact DC for details.

4 Validation characteristics

4.1 Scattering of measured values for samples

Reproducibility depends on, amongst other things, the quality of the sample matrix, its composition, volatility and the diffusion properties of the emittents.
The result also depends on whether reproducible surefaces can be produced during preparation of the samples. This can be more difficult in an open-pore foam, for example, than in a compact plastics sample.

Experiences with numerous measurements of various materials show that a reproducibility of < 15% is generally achieved for the VOC value.

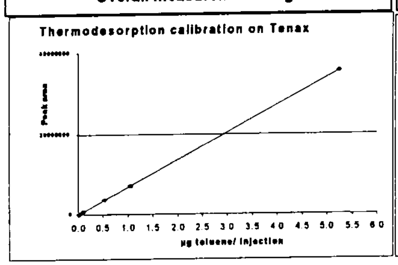
4.2 Limit of determination/linearity

The matrix-independent performance of the overall system is illustrated below by reference to the example of the linearity of toluene: defined amounts of toluene were analyzed according to section 3.3 and the statistical properties determined from the peak areas obtained.

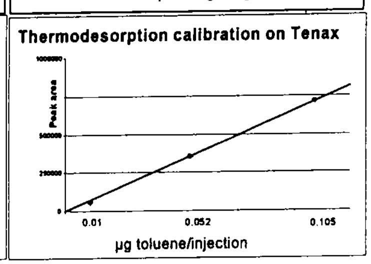
Graph 1 demonstrates the linear progression of the toluene response up to a high concentration zone (5 µg would correspond to approx. 150 ppm in a 30 mg sample).

Graph 2 illustrates the linear progression of three lower measuring points.

Graph 1 Linearity of toluene
Overall measurement range



Graph 2 Linearity of toluene
Lower operating range



The following correlation values are obtained from the overall data for this series of measurements:

$Y = a^1 X + a^0$ -	$a^1 = 6761000 \pm 48000$
	$a^0 = 10300 \pm 98000$
Correlation coefficient:	$r = 0.99998$

For the lower working range (VB = 95%)

Detection limit:	0.005 µg
Determination limit:	0.02 µg

Note:

1. The statistical characteristics were calculated according to DIN 38402 [10].
2. The determination and detection limits established here do not entirely reflect the conditions for an actual sample measurement. They are provided simply to help understand the minimum performance requirements for the analytical system.

4.3 Scattering and recovery of toluene

The toluene content was calculated from the control standard charged onto Tenax. The following measured values were obtained:

Number of measured values:	N =20
Number of measurement series:	6
Standard deviation	5.4 %
Mean recovery value (Actual/nominal value x 100)	102 %
Maximum recovery value	117 %
Minimum recovery value	85 %

The series of measurements was conducted over a period of approximately 6 weeks.

[10] Determined with: SQS software for statistical quality control of analytical data, PERKIN-ELMER

5 Possibilities for error, known problems

5.1 Sample preparation

When preparing the samples it is important to avoid any contamination or unnecessary heating of the samples. The samples must not be touched with the fingers or cut using heat-generating cutting techniques (e.g. high-speed circular saws).
The use of scalpels, tweezers, cork borers or scissors or pliers for harder samples is usually sufficient.
Cutting, weighing and transfer of the sample into the desorption tube must be done quickly. The charged desorption tube must be placed immediately into the autosampler feeder to avoid emission losses.
The specific surface area of the sample also has a significant influence, so its preparation should be made as reproducible as possible. Generally speaking, a higher level of emissions is obtained with a larger sample surface area. However, since the VOC/fog value always relates to the weighed amount, not to the surface area, and substances can behave differently in different matrices, this correlation is not entirely linear.

5.2 Incorrect substance identification

Misinterpretations can sometimes occur if substances cannot be separated or can only just be separated with the chosen analysis parameters. In particular, if substances with large concentration differences are eluted almost together, the smaller peak can easily be overlooked.
Examples (with no claim to completeness):

Ret. time (VOC)	Substances	Mass fragments	Comments
6.5 min.	Benzene/ methylcyclopentane/ n-butanol	78/ 69/ 31	
	Vinyl acetate /butadiene-1,3		Same mass spectra > risk of confusion! Distinction: ret. time is approx. 3.1 min. for butadiene-1,3 and approx. 4.2 min for vinyl acetate
13 9 min	o-xylene Cyclohexanone Butyl acrylate	91 98 73	Small amounts of cyclohexanone can sometimes be detected if the p/m xylene MS is subtracted from the o-xylene MS.
12.7 min	p+m-xylene Acetamide, N,N,-dimethyl Methoxypropyl acetate	91 44 72 87 43 58 72 87	

The guideline mass fragments listed here can also be used to check the particular substance by means of ion extraction.

5.3 Known Problems with the cold injection system (CIS, Gerstel)

It has been noticed that highly volatile substances (including toluene) can leak if the CIS liner is not adequately packed with silanized glass wool. This then has an influence on the calibration that is not immediately obvious.

If the semi-volatile substances display small pre-peaks during analysis of the control mixture (from around decane onwards), there is a strong possibility that a leak has occurred.

=> Remedy: pack additional glass wool loosely into the liner.

Increasing the amount of glass wool can also increase the peak areas and so produce better sensitivity. It also means that when the liner is changed the system will have to be recalibrated.

F Attention:
If liners are packed too tightly, the flow of carrier gas may not be able to be sustained in some circumstances (pressure increases).

5.4 Samples with a high water content

If very large quantities of water can be emitted from samples, there is a possibility that the liner, which has been cooled to –150°C, will freeze partially or entirely during desorption.
=> Result:
Values too low or analysis aborted completely (pressure increase too great).
This effect occurs in some circumstances in the case of samples containing leather or natural fibers.

=> Remedy: reduce weighed amount.

Appendix 1 to the DaimlerChrysler Test Instructions PB VWL 709

Weighed amounts of various materials for thermodesorption analysis

(Analysis of emissions of volatile and condensable substances from vehicle interior materials)

Unless otherwise specified, the standard weighed amount of samples is 30 ± 5 mg. The weighed amount generally applies to strip-shaped samples cut to size with a scalpel. The weighed amount has been specified for the following materials:

Material type	Weighed amount mg	Comments
Foam	15 ± 2	Material should be placed in the tube as loosely as possible and without being compressed. The influence of the weighed amount can be very high in the case of foams, which is why such narrow margins are necessary. **Sampling point:** on the surface of the foam (due to the possible influence of release agents).
Fiber composites (SMC, carbon fibers, etc.)	60 ± 20	Thicker sheets are usually split through the layer
Film-type samples	30 ± 5	Weigh out as individual strips where possible
Leather	10 ± 2	To obtain a more realistic measure of the influence of the wear surface of the leather and to take into account the effects of any protective coating that may have been used, part of the fabric side must be removed in the case of thicker leather samples. This also reduces the risk of the cryogenic trap freezing in the case of leather samples with a high water content. The following also applies until further notice: If the cryogenic trap still freezes when the method set out above is used, the weighed amount can be halved.
Paints	Calculated as shown	Paints are applied to aluminum foil and dried according to standard conditions. Film thickness: 50 ± 5 µm. Strips measuring 30mm x 3mm are cut from the film, weighed out and analyzed (the basic weight of the aluminum has to be deducted from the weighed amount). See also continuation sheet 2.
Adhesives/ composites etc.	30 ± 5	Where possible, weigh out in the form of strips of film of the same thickness used for the application (applied to aluminum foil)

Reasons for deviating from the specified weighed amounts must be logged.

Appendix 1 to the DaimlerChrysler Test Instructions PB VWL 709

Weighed amounts of various materials for thermodesorption analysis

(Analysis of emissions of volatile and condensable substances from vehicle interior materials)

Procedure for multilayer sandwich samples:

In order to keep costs to a minimum, it is permissible to analyze multilayer sandwich constructions together.
If the individual layers are relatively thick (over approx. 0.5 mm), the material in each layer should be analyzed separately. This is also useful in order to be able to allocate the emitted substances accordingly and to introduce targeted corrective action.
In addition, the results obtained are more reliable as the emission values can be related to the relevant individual material and the ratio of the thickness of the various layers can be disregarded during preparation of the samples (=> better comparability for material development).

If uncertainties are likely to arise as a consequence of the sample construction, each component must be analyzed separately (e.g. thin adhesive film on the surface of thick layers of foam).

In isolated cases it may be useful and possible to analyze the entire cross-section of the sample. This is done by punching out a core sample (diameter = 3 mm) from the entire cross-section of the sample and cutting it in half lengthways. Half core samples from different places are analyzed.

Other methods of sample preparation can also be established if necessary for specific components. The chosen method of sample preparation must be stated in the results report.

Appendix 2 to the DaimlerChrysler Test Instructions PB VWL 709

Production of paint films for thermodesorption analysis

(Analysis of emissions of volatile and condensable substances from vehicle interior materials)

To ensure comparability and consistency of measured values, the paint drying conditions must be defined and matched as closely as possible to standard production.
Standard conditions in the paint shop must also correspond to the instructions for use issued by the paint supplier.

The following procedure has been established for the production of paint films:

› The paint is sprayed onto a clean sheet of aluminum foil of size DIN A5 and a maximum of 30 µm thick. Dry film thickness: 50µm ± 5 µm (deviating from standard production if necessary).

› After being allowed to dry briefly (similar to standard production), the wet paints are stoved in a laboratory drying oven. The exact stoving temperature must be measured using a thermocouple positioned at the same height as the sample, and documented.

› Different types of samples must not be placed in the drying oven at the same time. To avoid contamination, the oven must be heated for at least two hours at 200°C before use.
Once preheated to the reference temperature (± 1.5 K), the oven may be opened only briefly to insert the samples.

› Loading the oven:
- Samples should be loaded on one rack level only (middle rack level)
- Oven operation: Partial air circulation at maximum circulation rate (> 10 [1/min])
  10 ± 5 % fresh air supply
- Oven load: 1 ± 0.2 [1/m]

Example:
a. Oven volume = 0.13 m^3
b. Paint area = 0.12 m^2 (equivalent to 4 DIN A5 sheets)
c. Oven <u>load</u> = 0.12m^2 /0.13 m^3 ≈ 1 [1/m]

The surface area of the samples must be adjusted accordingly if the oven volume differs from that in the example.

› Oven drying time and oven temperature:
The stoving temperature and time to be used are calculated as the mean of the upper and lower limit of the processing range as stated in the instructions for use issued by the paint manufacturer.

The actual drying temperature and drying time must be logged and stated in the sample approval report. The samples for standard monitoring must be produced under the same temperature/stoving time conditions

› On removal from the drying oven, the paints should be allowed to dry for 24 hours at room temperature (max. 23 °C). The surface of the paint must then be covered with aluminum foil and the samples packed into an airtight PE bag and sent to the analysis laboratory.
Alternatively the samples can be stored after packing for up to 14 days at a maximum temperature of –18°C before being dispatched.

› VOC/fog analysis in the laboratory (test instructions PB VWL 709)

The component supplier must submit a VOC/fog result from the Institut Fresenius for the first sample test report. This analysis may also have been commissioned by the paint manufacturer. This analysis must be no more than three years old and must relate to the current formulation. The shorter and cheaper analysis method in which only the total VOC or fog value is measured (see DB VWT 709) is sufficient for the standard monitoring required.

The analysis laboratory takes two 30 mm x 3 mm strips from the painted foil, weighs them and transfers them immediately to the thermodesorption tubes.
The basic weight of the aluminum foil must be deducted from the overall weighed amount to determine the actual weight of the paint. The analysis must therefore be provided with a blank sample of the aluminum foil used.
Further analysis is performed in accordance with the procedure set out in test instructions PB VWL 709.

Notes on standard painting:
Since the amount of solvent remaining in the paint film depends substantially on the drying conditions (particularly the temperature), compliance with the specified reference temperature is essential. Otherwise there is a risk that emissions in the vehicle interior may be higher.

Preparation of samples for wood paints

The film thickness of wood paints used in vehicle interiors is generally very large (approx. 800 µm).
This type of paint is therefore treated not as a "paint" (=> 50µm film on aluminum) but as a plastics sample.

The wood paints are applied to aluminum foil and dried in accordance with standard production conditions.
Film thickness: 800 ± 50 µm,
Aluminum foil thickness: 30µm (smooth surface).
Surface area: approx. DIN A4

The laboratory cuts a square piece from the painted foil measuring 10 mm x 3 mm (weighed amount: 30 mg ± 5 mg), weighs it **without aluminum foil** and transfers it immediately to the thermodesorption tubes for analysis.

Anlage 3 zur DaimlerChrysler-Prüfanweisung PB VWL 709

Chromatogramm-Reportausdruck im Excel-Format (Muster)

Thermodesorptionsanalyse

File :	10991A.D	**VWT-Nr. :**	
Pfad:	C:\HPCHEM\1\DATA\2000#5\	Externe Nr. :	1000_99/1001
Operator:	Kt	Wareneingang:	10.12.2000
Datum:	10.05.2000 00:00	Probenahme :	12.12.2000
Methode:	VOC	**Prod.Datum :**	
Probe :	**Musterbauteil, PUR-Folie DCX2000, Ch-Nr 444000555**		
Info:	**Musterlieferant, LxBxH 3x3,5x0,5mm 30,3 mg**		
Rohr-Nr. :	4	DC-Sach-Nr	99900888

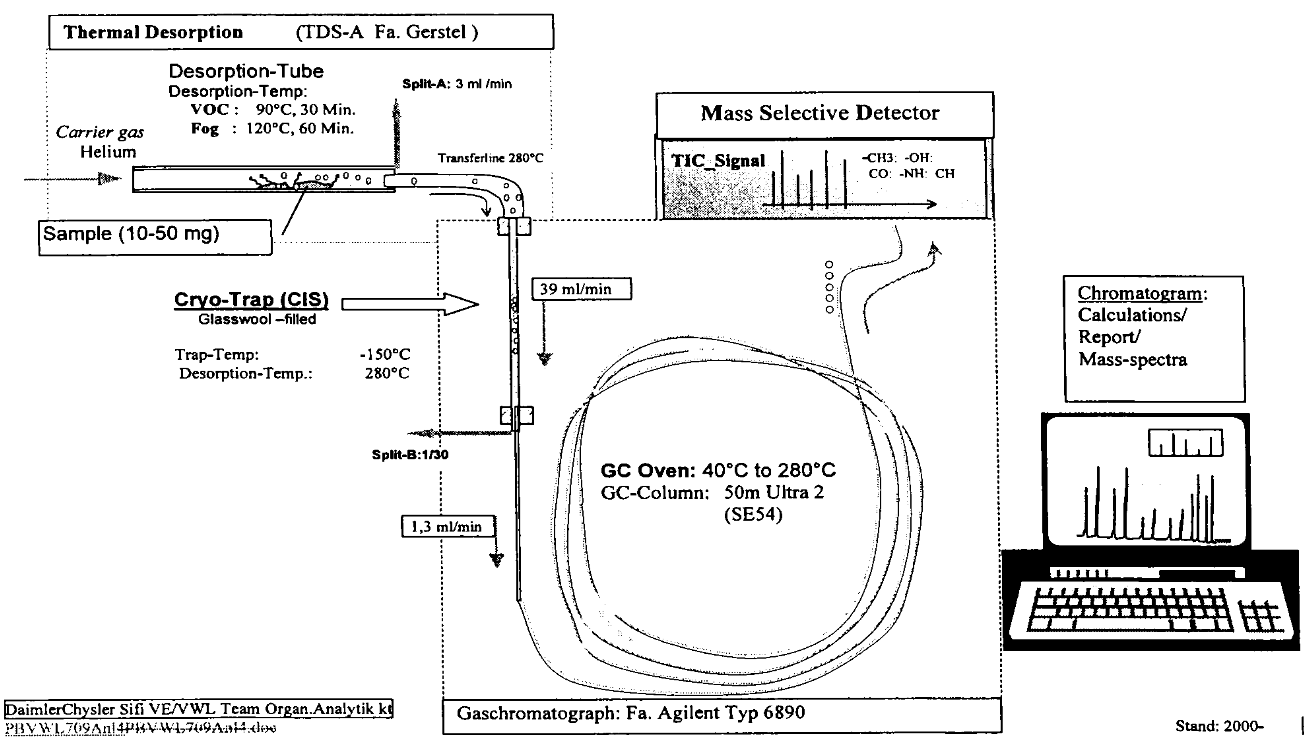
VOC

Höchstwert	**258**	ppm
Zweitwert	241	ppm

Retention Time(min.)	Substanzname	CAS-Nr.	Flächen(%)	ppm	Bewertung
3,82	2-Propanone (CAS) $$ Aceton	000067-64-1	0,5	**1,4**	
5,05	Acetic acid (CAS) $$ Essigsäure	000064-19-7	0,8	**2**	
19,22	1,3-Dioxolan-2-one (CAS) $$ Ethylene carbonate	000096-49-1	0,7	**1,7**	
21,97	? Massen 73 99 105	000000-00-0	0,4	**0,9**	
22,38	2-Ethyl-1-hexanol = "Isooctanol" = Isooctylalkohol	000104-76-7	0,4	**1,0**	
43,14	Öl (Isoalkane), Ret. 35 - 50 Min., Siedebereich ca. C14-C20		97,3	**251**	
	Summe der identifizierten oder zugeordneten Substanzen		100	**258**	

Bemerkung:

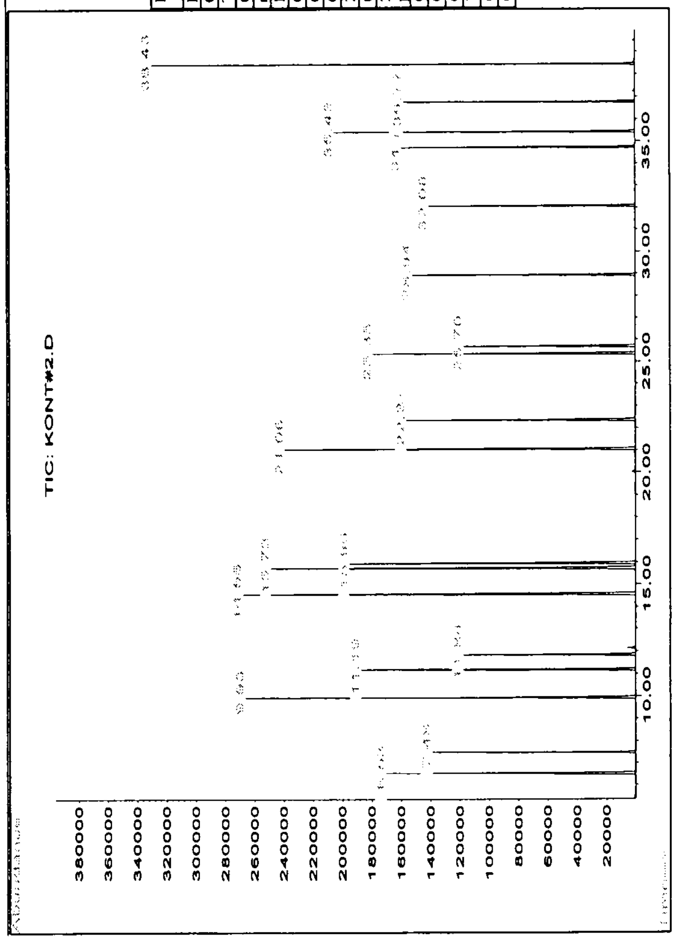
Anlage 4 zu DaimlerChrysler-Prüfanweisung PB VWL 709 **Skizze Thermodesorptionsanalyse**



Anlage 5 zu DaimlerChrysler – Prüfanweisung PB VWL 709

Gaschromatogramm Kontrollmischung

Komponente	Ret-Zeit	Area	µg
Benzol	6.53	5124785	1,14
C7	7.48	3228221	0,91
Toluol	9.93	7632681	1,18
C8	11.19	5286993	0,96
n-Butylacetat	11.84	3416400	1,23
P/M-Xylol	14.56	9023794	1,18
O-Xylol	15.73	8508487	1,21
C9	15.96	6383404	1,00
C10	21.06	7521075	1,26
2-Ethylhexanol	22.37	4778433	1,12
C11	25.35	5023323	1,03
2,6-Dimethyl-phenol	25.70	3540155	0,64
C12	28.94	4120018	1,03
C13	32.08	3710219	1,04
C14	34.74	3411878	1,04
Dicyclohexylamin	35.43	4726648	1,23
C15	36.77	3224551	1,04
C16	38.43	6094852	1,95



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Sindelfingen Plant

Appendix 6 to the DaimlerChrysler Test Instructions PB VWL 709

(Analysis of emissions of volatile and condensable substances from vehicle interior materials)

1 Limiting values/target values

The following requirements apply with immediate effect:

1.1 Total emissions

VOC value	Target value: ≤ 100 ppm
Fog value	Target value: ≤ 250 ppm

F **These requirements do not apply to the <u>material-specific</u> limiting values for VOC and fog as specified in the relevant DBLs.**

1.2 Limiting values for individual substances for VOC and fog analysis

Corresponding to the categories in the latest MAC list published by the DFG[1]		
Carcinogenic	K1 K2, K3 A K3 B	≤ 1 ppm = 3 ppm = 8 ppm = 8 ppm
Pregnancy	A B	≤ 1 ppm ≤ 3 ppm
Mutagenic	1 2, 3 A 3 B	≤ 1 ppm ≤ 3 ppm ≤ 8 ppm ≤ 8 ppm
Allergic effect	H, S	Target: ≤ 8 ppm

[1] From the latest edition: List of MAC and BAT values
Deutsche Forschungsgemeinschaft
Senatskommision zur Prüfung gesundheitsschädlicher Arbeitsstoffe
Wiley-VCH Verlag GmbH, D-69451 Weinheim, Germany

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